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IMPROVEMENT IN THE STABILISATION OF
HALOVINYL RESINS

Abridgement

Improvement in the stabilisation to heat, shock and light
of resins incorporating a halogen.

In addition to a metal compound, an organic acid ester is
incorporated in the resin, in which the mercaptan function
is joined to a carbon atom of the alcohol residue of this
ester.

An important application is the stabilisation of polyvinyl
chloride or modified polyvinyl chloride.

IMPROVEMENT IN THE STABILISATION OF HALOVINYL RESINS

The invention disclosed in the following description relates to the stabilisation of halogeno-vinyl resins with respect to heat. It relates more particularly to an improvement in the stabilisation by the addition of metal derivatives, particularly those of tin, antimony, zinc, magnesium or other alkaline earth or alkali metals. The invention relates particularly to additives which, in conjunction with metal compounds, make the resin more resistant to heat and to shock, as well as more stable to light. It also comprises a process of preparation of these additives.

In view of the considerable importance of vinyl resins, particularly those comprising polyvinyl chloride, the stabilisation of these resins has been the subject of considerable study. It is in practice necessary to inhibit the undesirable effects which heating has on halogeno-vinyl polymers, in order to be able to effect safely various hot forming operations on these plastics materials. Stabilisation by the addition of various tin compounds is well known and has given rise to an abundant literature. The compounds which have given considerable satisfaction are organic derivatives containing both tin and sulphur. However, as they do not allow the Sn/S ratio to be varied according to needs, there has been a tendency to replace them with mixtures of tin compounds with organic additives, usually sulphur containing. Thus, various systems constituted by a mixture of one or more tin compounds with mercapto or thio compounds have been proposed. For example, according to German Patent 1 217 609, the stabiliser comprises a mixture of mono- or di-organotin with a mercapto ester. US Patent 3 063 963 utilizes a mercapto acid or a mercapto alcohol with a di-organotin compound. These compounds are replaced by a

thio-ether in accordance with US Patent 3 297 629. Other patents describe the addition of substances such as thio-anhydrides, mercaptols, mercaptals, aliphatic mercaptans or organic di-sulphides. In a general manner, when the additive contains a mercaptan function, according to the prior art, the sulphur atom is always located in the acid residue, that is to say in the chain connected to the carbon atom of the carboxylic group.

The various systems proposed up till now have disadvantages either because of their insufficient efficacy, as is the case with sulphides or di-sulphides or of too strong an odour, as occurs with esters of thio-glycolic acid, with mercapto alcohols or others, or because of the high cost of the products utilised, in particular in the case of anhydrides of thio-acids.

The present invention results from the unexpected confirmation that the disadvantages indicated above can be suppressed and that an excellent stabilisation of resins containing a halogen, particularly halogeno-vinyl resins, can be obtained by the use of certain additives, different from those which have been suggested for use up till now. The Applicants have found that it is possible to have with a sufficiently low market price, sulphur-containing esters which are very efficacious in application in conjunction with metal compounds and they do not release any odour. Moreover, these new additives have a more favourable effect upon the viscosity of the resin at working temperatures than other known stabilising systems. They also allow good lubrication of the product during working which facilitates the flow of the resin. Resins containing a halogen to which the invention relates can be homopolymers, for example polyvinyl chloride, polyvinylidene chloride, polychlorotrifluoroethylene, polytetrafluoroethylene, polychloro-ether, polydichlorostyrene, etc., copolymers such as poly-

vinyl acetochloride or others or combinations or various mixtures, for example polyvinyl chlorides modified with ethylene and/or with propylene, acrylonitrile-butadiene-styrene, ethylene/vinyl acetate and similar polymers.

The new additives according to the invention are alkyl organic esters containing a mercapto group in the alcohol residue of the ester. These compounds can be represented by the general formula:



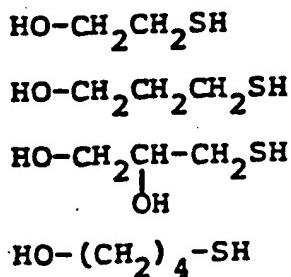
in which R is a linear or branched alkyl or alkenyl, aryl or aralkyl, containing at least two carbon atoms and preferably 6 to 38, most preferably 8 to 18, this radical also possibly carrying a second carboxylic group which may or may not be combined with a second -R'SH group; R' designates a C₂ to C₁₈ alkylene, preferably C₂ to C₆, this alkylene can advantageously also carry one or more -OH.

Thus, contrary to the various mercapto esters of the prior art in which the -SH function is located in the acid residue, that is to say in the chain which corresponds to R in the above formula, the products according to the invention are characterised in that they carry their mercapto group in the alcohol residue, that is to say in the R' chain. It is surprising that due to this difference of the position of -SH the activity of the ester vis-à-vis tin stabilisers is profoundly modified to the point of suppressing the disadvantages noted above and providing a remarkable efficacy. There are in addition the advantages of the facility of preparation and purification of these bodies as well as the absence of odour.

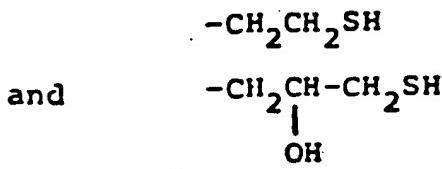
While the R radical in the esters according to the invention can in practice comprise any aliphatic mono- or di-acid, the preferred esters are derived from fatty acids, particularly caprylic, pelargonic, capric, undecanoic, lauric, myristic, palmitic, stearic, isostearic or a mixture of such acids. Excellent stabilisers are obtained by the addition of a mixture of palmitic and stearic esters of an alkylene mercaptan to a tin stabiliser of known type. Esters of aryl acids, for example benzoic, benzylic, phenyl-acetic, phenyl-propionic etc. are also suitable.

As mentioned above, the ester according to the invention can be a mono- or di-ester of a carboxylic di-acid. Suitable esters are for example those of succinic, adipic, di-oleic, phthalic ester acids etc.

The alcohol residue which according to the invention is a residue of a mercapto alcohol can be derived from various mono- or poly-alcohols carrying a thiol group, for example:



these examples being non-limitative. In practice for economic reasons, the mercapto ethyl esters and those of thioglyceryl are particularly suitable, that is to say esters in which the -R'SH group is respectively



The more the molecular weight of the ester is raised and the lower the vapour pressure of the compound, this diminishes any risk of odour.

The addition of the esters according to the invention to tin compounds permits very substantial reduction of the quantity required of the latter which constitutes a considerable saving. This saving can range from 20 to 95% of the quantity of tin to be used with respect to stabilisation with tin compounds alone.

The invention also gives excellent results in the stabilisation of halogeno-vinyl resins with stabiliser systems for polyvinyl chloride other than stabilizers based on tin. Systems such as those derived from alkali metals (sodium, potassium), alkaline earth metals (calcium, barium) and other metals, such as magnesium, zinc, antimony or their mixtures or with various other additives are particularly suitable. These additives can be in particular the epoxides, for example epoxidized soya oil, phosphites, particularly triphenyl phosphites and antioxidants such as tert.butyl catechol and others. When using alkali or alkaline earth metals and/or zinc, the metal derivatives which are particularly suitable are the carboxylates. Reference can be made in a non-limitative matter to the laurate, stearate, benzoate, caproate, caprylate, 2-ethyl-hexanoate, naphthenate, neoalkanoate and oleate. However, a certain number of derivatives such as the carbonate, oxide, sulphate can also be advantageously used.

When antimony is chosen as the metal, particularly advantageous results are obtained when the additives R-COOR'SH are employed in conjunction with antimony trimercaptides, these trimercaptides being derived desirably from aliphatic mercaptans, esters of mercapto-acids or esters of mercapto-alkyls.

The metal derivatives and/or the additives can be incorporated in the resin in proportions which can range from 0.01 to 5% by weight of the resin employed. The esters R-COOR'SH can be utilised in proportions ranging from 0.1 to 5% by weight of the resin, in particular from 0.5 to 2%.

Application of the stabiliser mixtures according to the invention in an identical stabilising proportion allows a saving of 20 to 95% of the quantity of metal derivatives necessary, with respect to the same metal derivatives employed without the R-COOR'SH additives.

The new additives allow reduction of the discolouration of resins during heating. They also permit counteraction of the increase in viscosity which is caused by the addition of tin stabilisers. These two effects can be obtained simultaneously. It is an important advantage, particularly as known tin stabilizers are not capable in general of producing these two effects together. Certain of them are effective in reducing discolouration and others in regulating viscosity. It is remarkable that these results can be obtained as well with mono- or di-organic tin derivatives, with salts of tin not containing sulphur and with those which also contain the latter or with their mixtures.

The new additives can be incorporated in the resin after polymerisation but before drying of the polymer or also at the time of use thereof.

The new additives can be prepared by the direct action of an aliphatic acid on a mercapto-alkanol in the presence of an acid within a hydrocarbon serving as a solvent.

The invention is illustrated non-limitatively by

the Examples which follow.

EXAMPLE 1

Synthesis of mercapto-ethyl stearate $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{CH}_2\text{CH}_2\text{SH}$

284g, namely 1 mole of stearic acid, 86g or 1.1 mole of 2-mercaptop-ethanol, 0.8g paratoluene sulphonic acid and 200 ml of benzene were introduced into a 1l flask, provided with an agitator device, a DEANSTARK separator and a condenser. The whole was heated under nitrogen until a good reflux was established, without exceeding 100°C in the liquid. Heating under reflux was continued for about 6 hours, to effect esterification of the stearic acid. 200 ml of benzene was then added to the reaction medium. After cooling, it was washed twice with 200 ml of water both times.

The benzene was evaporated under reduced pressure, which left 330 g of the crude ester of mercapto-ethyl stearate, the latter titered 9.2% SH, compared with 9.6 in theory.

EXAMPLE 2

Synthesis of 3-thio-glyceryl myristate $\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2-\text{CHCH}_2-\text{SH}$
|
OH

The mode of operation of Example 1 was employed using 228 g or 1 mole of myristic acid to which was added 216 g that is to say 2 moles of thio-glycerol, 2 g of para-toluene sulphonic acid and 500 ml of benzene.

The esterification was arrested when 1 mole of water had been recovered. The reaction medium was then washed 3 times with 500 ml of water. After evaporation of the benzene under pressure, 322 g of a crude ester of 3-thio-glyceryl myristate was recovered, titering 8.4% SH as against 10.4% in theory.

EXAMPLES 3 to 6

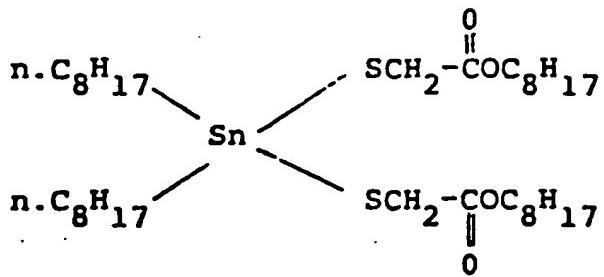
In these examples, samples of polyvinyl chloride stabilised with the additive according to the invention were subjected to colouration tests on heating. For this, a composition was mixed at 180°C on a roller mixture, the composition comprising:

100 parts by weight of polyvinyl chloride known under the commercial name LACQVYL SQ71S having a coefficient of viscosity K=56

0.5 parts of "E" wax constituting an external lubricant

x part of the stabiliser of the nature and quantity indicated in each of the examples.

The results obtained were compared with those obtained with the standard stabiliser known to be effective, di-n.octyltin-bis-(isoctyl-mercapto-acetate).



Discolouration of the resin was observed in each case and the time in minutes was noted from when the product began to discolour and that which corresponded to browning of the sample.

In each of the examples of this group, a table of results is given in which are indicated the percentage proportions by weight of the stabiliser and the additive with respect to the polyvinyl chloride. Two other columns indicate the time of discolouration mentioned above.

EXAMPLE 3

The tests were effected in part with the standard stabiliser of the formula given above in various proportions and in part with the same stabiliser containing mercapto-ethyl stearate described in Example 1.

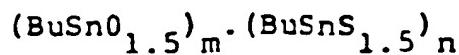
The following results were confirmed:

	%	<u>Discolouration</u>	
		<u>Beginning</u>	<u>Browning</u>
Tin stabiliser alone	0.07	2'	5'
	0.25	4'	9'
	0.35	7'	12'
	0.70	11'	25'
The same stabiliser	0.07)	
)	
+ mercapto-ethyl)	
stearate	1.00)	9'

It can be seen that the addition of 1% of the stearate to polyvinyl chloride allows reduction of the discolouration at 180° in the presence of only 0.07% of the standard stabiliser as good as if employing 0.25% of the latter alone. There is thus a saving of 72% of the expensive tin stabiliser, while the mercapto-ethyl stearate is a less costly substance. This saving is even larger with respect to industrial cases where 1% or even more of the tin stabiliser is used.

* EXAMPLE 4

The standard stabiliser tested here was a condensation polymer of butyl stannic and butyl thiostannic acids which can be represented by the formula



<u>Discolouration</u>			
	<u>%</u>	<u>Beginning</u>	<u>Browning</u>
Stabiliser with tin alone	0.1	8'	12'
" " "	0.02	4'	6'
Same stabiliser	0.1)		
+ mercapto-ethyl stearate) 1.00)	16'	25'
Same stabiliser	0.02)	7'	12'
+ the same stearate	1.00)		
Stearate alone	1.2	immediate	3'

These results show the very marked effect of mercapto-ethyl stearate in retarding discolouration. Thus with 1% of the stearate it is sufficient to utilize 0.02% of the tin stabiliser to have a result as good as with 0.1% of the latter. There is thus a gain of 80% in tin by utilization of the stearate according to the invention. The latter horizontal line of the table shows that the effect of the ester added must be due to an unexpected synergistic phenomenon, since the mercapto-ethyl stearate alone has no retarding action on discolouration of polyvinyl chloride under heating.

EXAMPLE 5

The standard stabiliser tested was butyl stannic acid $BuSnO_2H$ and the stearate added was the same as in the preceding example.

<u>Discolouration</u>			
	<u>%</u>	<u>Beginning</u>	<u>Browning</u>
$BuSnO_2H$	0.05	immediate	10'
" "	0.05)		
+ stearate	1.00)	12'	25'

With butyl stannic acid alone it is not possible to obtain a stabilisation as good as that obtained by the addition of the stearate. It will be noted that the latter result is equivalent to that given by the iso-octyl-mercapto-acetate stabiliser of the formula given above in an amount of 0.7%. There is thus a gain in weight of tin or more than 75% by the addition of the stearate.

EXAMPLE 6

The same tin stabiliser as in Example 5 was tested in conjunction with 3-thio-glyceryl myristate at a ratio of 0.05% of the former and 1% of the latter. Discolouration began after 5 minutes and browning began at 12 minutes. There is thus a very marked improvement due to the addition of the myristate since butyl stannic acid alone gives rise to an immediate commencement of discolouration and browning after 10 minutes as can be seen from Example 5.

As regards browning, this result with the myristate is equivalent to that of the tin stabiliser alone in Example 3 at a rate of 0.35%.

EXAMPLES 7 to 9

These examples illustrate the favourable effects of the additives according to the invention on the viscosity of polyvinyl chloride. The relevant determinations were effected by means of the known Brabender apparatus which is a rotary rheometer. This apparatus registers formation of the mixing couple of the resin at a given temperature as a function of time (it is described for example in *Plastiques Modernes et Elastomères*, March 1975).

The measurements were carried out on the known polyvinyl chloride resin marketed under the commercial name

S 111 having a viscosity constant $K = 67$. The resin incorporated certain agents in the following proportions:

Polyvinyl chloride	100 parts by weight
CaCO_3	3 " " "
TiO_2	1 " " "
"E" wax	0.8 " "
Stabiliser system	in the proportions indicated in the examples.

The apparatus was operated at 200°C with a speed of rotation of the mixing rotor of 60 rpm.

Curves representing the force in m.kg as a function of the time in minutes starting from the 3rd minute are given in the accompanying drawings.

Fig. 1 is a Brabender diagram of a mixture of the known tin stabiliser.

Fig. 2 is a similar diagram obtained with the stabiliser of Fig. 1 incorporating also an additive according to the invention.

Fig. 3 is a Brabender diagram obtained with another known stabiliser alone and also containing an additive according to the invention.

Fig. 4 relates to a third stabiliser of known type.

Fig. 5 illustrates the results of Example 22.

EXAMPLE 7

The stabiliser of known type was a mixture of the anhydride of thio-butyl stannic acid with di-n.butyltin-bis(isodecyl-mercapto acetate).

In the diagram of Fig. 1, the Brabender curve 1

is plotted for polyvinyl chloride with 1.8% of the stabiliser mixture indicated above, while the curve 2 corresponds to 0.9% of the same stabiliser.

In Fig. 2, the three curves correspond to polyvinyl chloride containing the following percentages of the same standard stabilizer with also mercapto-ethyl stearate.

	<u>Stabiliser</u>	<u>Stearate</u>
Curve 3	0.9	1
" 4	0.9	2
" 5	0.45	2

It can be seen that the curves for the mixture containing the stearate, that is to say curves 3 to 5 have a slope systematically lower, by about 15%, than the curves 1 and 2 corresponding to the standard stabiliser alone. This signifies that the necessary power for working the resin is less when it contains an ester according to the invention. Since the advantage is clear, the rate of production can be increased.

Another result is that at an equal tin content systems containing the stearate (curves 3 and 4) are better as regards the shape and length of the plateau of the curves recorded. Thus curve 4 has a longer extent than curve 1, that is to say the system containing 0.9% of the tin stabiliser and 2% of the stearate (curve 4) is as good as that containing 1.8% of the same tin stabiliser alone (curve 1). Thus by adding the stearate there is a saving of 50% of the quantity of tin utilised.

Also, the curve 5 is even better than the curve 2, which indicates that 0.45% of the tin stabiliser with

2% of the stearate gives results better than 0.9% of the tin stabiliser alone.

It can be confirmed also that the curves 3 and 5 are equivalent, that is to say that 0.9% of the stabiliser with 1% of the stearate (curve 3) can be replaced by 0.45% of the tin stabiliser + 2% of the stearate (curve 5). Thus at the rate of increase of the stearate content, there can still be a saving in tin. Moreover, these curves 3 and 5 are not very different from the curve 1 at 1.8% of the tin stabiliser, which serves for a comparison within the present study.

It is also to be noted that the time of gelification of the mixtures according to the invention are similar or shorter than those of compositions containing only the known tin stabiliser.

EXAMPLE 8

The stabiliser of the known type, serving as a comparison in the tests illustrated by Fig. 3, is di-n.-butyltin-bis(isooctyl-mercapto acetate).

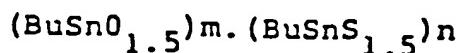
The curve 6 corresponds to polyvinyl chloride containing 2.2% of this butyltin derivative, while the curve 7 is related to a similar test, but with 1.1% only of the stabiliser and 1% of mercapto-ethyl stearate.

It can be seen that the two curves are practically equivalent which indicates a gain of 50% in the quantity of tin utilised which can be obtained due to the addition of the 1% of stearate. It will also be remarked that the curve 7 according to the invention is more regular, which signifies in practice that the mixture operates better.

EXAMPLE 9

Here the measurements were carried out on the polyvinyl chloride described above, also containing the

known stabiliser, constituted by a condensation polymer of butyl-stannic and butyl-thio-stannic acids.



In Figure 4, the Brabender curve 8 corresponds to polyvinyl chloride containing 0.37% of the above stabiliser alone. The curve 9 is that of the same resin to which has been added 0.37% of this known tin stabiliser together with 1% of mercapto-ethyl stearate. The curve 10 corresponds to 0.19% of the tin stabilizer and 2% of the stearate. It can be seen that the latter is better in all respects that is to say that it has about half the tin stabiliser and yet obtains results which are better if sufficient stearate is added.

EXAMPLE 10

The measurements analogous to those of Example 7 were effected with mercapto-ethyl-palmitate as the additive to the tin stabiliser, in place of the corresponding stearate.

The Brabender curves present the same form as curves 3 to 5 in Figure 2 and were quantitatively very close to the latter. Thus, with 1% of mercapto-ethyl-palmitate and 0.9% of the tin stabiliser, a couple of 1.4 m.kg was obtained in 20 minutes.

EXAMPLE 11

The palmitate of Example 10 was replaced by mercapto-ethyl myristate, the Brabender diagrams still having the same shape. At 20 minutes a couple of 1.35 m.kg was found.

EXAMPLES 12 TO 14

In these examples, samples of polyvinyl chloride

containing various stabilisers were subjected to discolouration tests on heating. For this, the composition was mixed for five minutes at 180°C on a waterbath, containing:

roll mill

100 parts by weight of polyvinyl chloride, known under the commercial designation LACQVYL S/071/S having a viscosity coefficient K = 56,

x parts stabiliser,

0.5 parts "E" wax (ester of montan acid) which constitutes the external lubricant. The sheet of PVC so obtained was cut into pieces 2 x 1 cm. These pieces were heated at 204°C in an oven (thermostated) and they were inspected every five minutes.

The colour of the samples inspected varied according to the stabiliser utilised and with time.

The results are set out in the following tables:

EXAMPLE 12

Stabiliser x :)	0.6 parts of calcium stearate
) <u>0.4 parts of zinc stearate</u>	

Time of heating to 204°C (in mins)	0	5	10
Colour:	red	yellow	black

EXAMPLE 13

Stabiliser x :)	0.6 parts calcium stearate
) <u>0.4 parts zinc stearate</u>	
) <u>1 part mercapto-ethyl stearate</u>	

Time of heating to 204°C (in mins)	0	5	10
Colour:	white	very clear yellow	black

EXAMPLE 14

Stabiliser x :)	0.6 parts calcium stearate
)	0.4 parts zinc stearate
)	<u>2 parts mercapto-ethyl stearate</u>

Time of heating to 204°C (in mins)	0	5	10
Colour:	white	white	black

These tables show that the addition of mercapto-ethyl stearate improves the initial colour of the polyvinyl chloride after 5 minutes of heating. In contrast the crude decomposition of polyvinyl chloride after 10 minutes of heating, connected with the presence of zinc, is not improved.

EXAMPLES 15 and 16

Operating as in the foregoing examples, epoxidized soya oil was added to the mixture however.

EXAMPLE 15

Stabiliser x :)	0.6 parts calcium stearate
)	0.4 parts zinc stearate
)	<u>4 parts epoxidized soya oil</u>

Time of heating to 204°C (in mins)	0	5	10	15	20
Colour:	red	yellow	yellow brown	black	brown

EXAMPLE 16

Stabiliser x :)	0.6 parts calcium stearate
)	0.4 parts zinc stearate
)	4 parts epoxidized soya oil
)	<u>1 part mercapto-ethyl stearate</u>

Time of heating to 204°C (in mins)	0	5	10	15	20
Colour:	White	very clear	clear	yellow yellow	black

Introduction of the methyl stearate clearly improved the stability to discolouration.

EXAMPLES 17 to 21

Operation was as in the foregoing examples, but with antimony derivatives in place of the calcium and zinc derivatives.

The stabiliser was either $Sb(SCH_2CO_2\text{-isooctyl})_3$ shortly called $Sb(IOTG)_3$, utilised alone or a mixture of this antimony salt with various proportions of mercaptoethyl stearate.

Discolouration of the resin was observed in each case and the time in minutes was noted from the start in which it was produced and that which corresponded to browning of the sample.

In each of these examples, a table of the results is given in which are indicated the proportions in percentage by weight of the products which composed the stabiliser, with respect to the polyvinyl chloride.

Stabiliser	x parts		
		clear yellow mins	dark yellow mins
$Sb-(IOTG)_3$ ex.17	0.07	2	12
$Sb-(IOTG)_3$ ex.18	0.17	4	18
$Sb-(IOTG)_3$ ex.19	0.35	8	27
$Sb-(IOTG)_3$ ex.20	0.07	6	38
+ stearate of M.E.	2	-	-
$Sb-(IOTG)_3$ ex.21	0.17	-	-
+ stearate of M.E.	1	8	35

This table shows that the degree of stabilisation obtained with 0.07 part of $Sb(IOTG)_3$ and two parts of mercaptoethyl stearate is practically equivalent to that obtained with 0.35 parts of $Sb(IOTG)_3$ alone. It has thus been possible for the same result to utilise 5 times less antimony.

EXAMPLE 22

This example shows the favourable effects of the stabiliser compositions according to the invention on the viscosity of polyvinyl chloride. The relative determinations were effected by means of the known Brabender apparatus, by the aid of which measurements were made of the evolution with time of the viscosity of a polyvinyl chloride resin.

The measurements were carried out on the known polyvinyl chloride resin marketed under the commercial name S111 having a viscosity constant K = 67. The resin included certain stabiliser agents in the following proportions:

Polyvinyl chloride	100 parts by weight
TiO ₂	1 " " "
CaCO ₃	3 " " "
"E" wax	0.8 " " "
mercapto-ethyl stearate	x " " "

The tests were carried out at 200°C with a 50g charge of polyvinyl chloride. The speed of rotation of the Brabender apparatus was fixed at 60 rpm. The curves of Fig. 5 show the couple in m.kg as a function of the time in minutes.

The curve 1 corresponds to a mixture without mercapto-ethyl stearate, the curve 2 to a mixture containing 1 part of this stearate and the curve 3 to a mixture containing 2 parts of mercapto-ethyl stearate.

It can be noted that the duration of the viscosimetric plateau is considerably augmented by the addition of mercapto-ethyl stearate, which constitutes a very large advantage for the transformation of the PVC. It is not possible to obtain such an improvement by the single increase of CaCO₃.

EXAMPLE 23

This example, carried out on an industrial sample, illustrates the interest there is in stabilising mixtures according to the invention for the fabrication of bottles of polyvinyl chloride (PVC) by blown extrusion. The machine utilised was of the "HESTA" type. The organotin derivative employed was the mixed anhydride of butyl stannic and butyl thio-stannic acids already described above in example 15.

Operation was on the following formulations in which the quantities are in parts by weight.

<u>Formulation No</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
PVC S 071 S	100	100	100	100	100	100
"Paraloid K 175" (internal lubricant from Rohm & Haas Co)	0.5	0.5	0.5	0.5	0.5	0.5
"E" wax	0.5	0.5	0.5	0.5	0.5	0.5
Mercapto-ethyl stearate	—	1	0.5	1	0.5	—
Tin derivative	0.3	0.2	0.2	0.1	0.1	0.2
"Loxiol G-12" (external lubricant)	—	—	—	—	—	1

The bluing agents generally utilised in formulations of this type have been voluntarily suppressed in order to adjudge the actual colour of the PVC. Three successive runs were carried out on the machine with the same PVC, by grinding and recycling the bottles. The result in order of efficacy of stabilisation was the following:

Formula 2 and 3, results substantially better than for formula 4;

The latter was better than 6;

6 was better than 5, this being virtually equivalent to control 1.

It can be seen with respect to the control formulation (No. 1) that the Sn content can be reduced to a third of its value by adding 0.5 part of mercapto-ethyl stearate (formulation 5), at a constant degree of stabilisation. The formulations 2, 3 and 4 containing a lower proportion of tin, respectively one third and two thirds of that of the formulation 1, gave clearly superior results.

The formulation 6 where the mercapto-ethyl stearate had been replaced by a lubricant confirmed that the role of the stearate is not simply to lubricate, but it also intervenes directly in the colour of the PVC.

CLAIMS

1. Improvement in the stabilisation to heat, shock and light of resins containing a halogen, by the addition of one or more metal compounds, which consists in incorporating also into the resin an organic additive having a mercaptan function, characterised in that this additive is an ester of an organic acid, in which the mercaptan function is connected to a carbon atom of the alcohol residue of the ester.

2. Improvement according to claim 1, which consists in incorporating the ester additive containing a mercaptan function in the alcohol residue in the resin stabilised with one or more metal compounds, characterised in that the proportion of the additive is from 0.1 to 5% and preferably 0.5 to 2% by weight of the resin.

3. Improvement according to claim 2, characterised in that the additive, which can be formed by several esters, is added to the resin simultaneously with the one or more metal compounds or separately.

4. Improvement according to any of claims 1 to 3, in which the metal compound is a derivative of tin, antimony, zinc, magnesium or other alkaline earth metal or an alkali metal.

5. Improvement according to any of claims 1 to 4, in which the resin includes an epoxide, a phosphite and/or an anti-oxidant.

6. Stabiliser additive for carrying out the improvement according to any of claims 1 to 5, characterised in that it is of the type $\text{RCOO}-\text{R}'\text{SH}$, where R is an alkyl or alkenyl containing at least two carbon atoms and preferably 8 to 18C, or an aryl or aralkyl, the R group possibly carrying a second carboxylic group or a second group $-\text{COOR}'\text{SH}$, while R' is a C_1 to C_{18} alkylene which can carry one or more $-\text{OH}$.

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7. Additive according to claim 6, characterised in that RCOO- is a fatty acid residue, in particular caprylic, perlargonic, capric, undecanoic, lauric, myristic, palmitic or stearic.

8. Additive according to claim 6, characterised in that the group RCOO- derives from an aliphatic diacid, in particular succinic, adipic or dioleic or an aromatic diacid, particularly phthalic.

9. Additive according to any of claims 6 to 8, characterised in that the group -R'SH is derived from a C₂ to C₆ mercapto alkanol, in particular 1-mercaptopropanol-2, 1-mercaptopropanol-3, 1-mercaptopropanol-2-hydroxypropanol-3 or 1-mercaptopropanol-4.

10. Additive according to claim 9, characterised in that it comprises calcium stearate and mercaptoethyl stearate.

11. Additive according to claim 9, characterised in that it comprises an organic tin compound and mercaptoethyl stearate.

12. Additive according to claim 9, characterised in that it comprises antimony tri-mercaptide and mercaptoethyl stearate.

13. A plastic mass of polyvinyl chloride or of modified polyvinyl chloride, stabilised by the process according to any of claims 1 to 5.

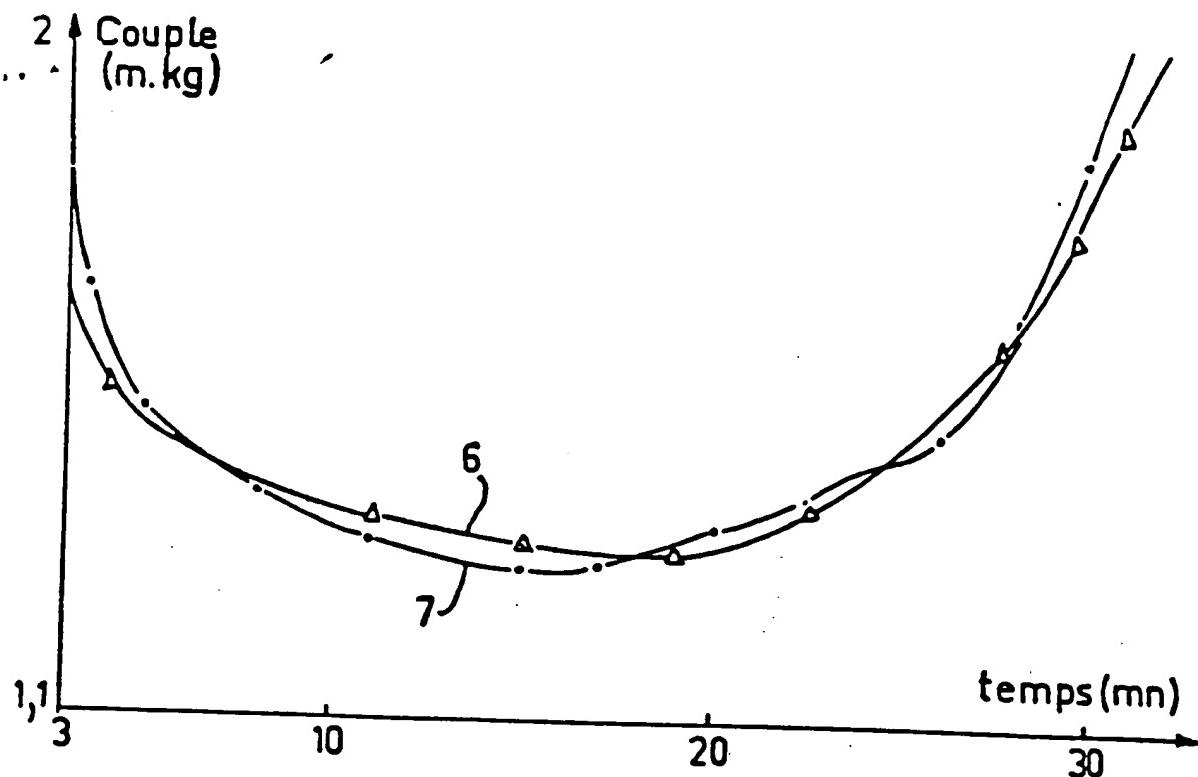


FIG.3

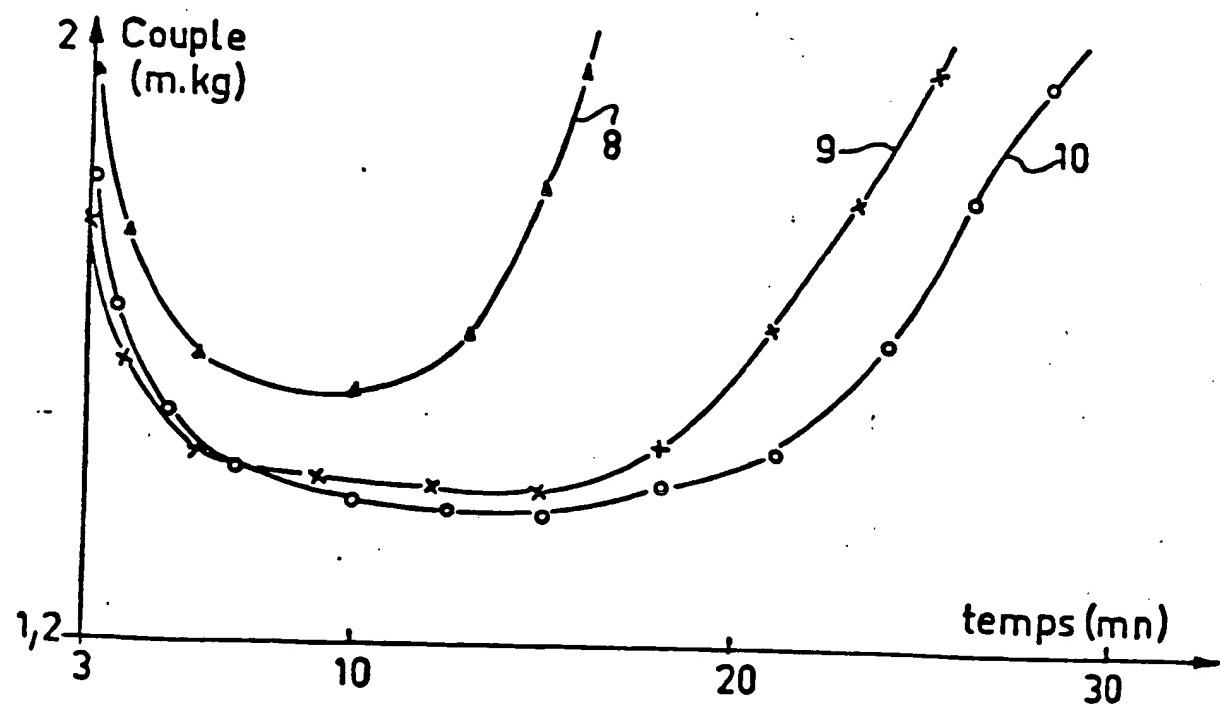


FIG.4